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(71) Applicant: **CHEMICAL RESEARCH &
 LICENSING COMPANY**
1603 Galveston Street
South Houston, Texas 77587(US)

(72) Inventor: **Smith, Lawrence A., Jr.**
1500 Strawberry Street Harris County
Pasedena Texas 77502(US)

(74) Representative: **Jukes, Herbert Lewis**
Swann, Elt & Company 31 Beaumont Street
Oxford OX1 2NP(GB)

(54) **Catalytic distillation.**

(57) A method of carrying out chemical reactions in a reaction-distillation column, wherein the materials of a reaction mixture are separated by distillation, the method being used with reactants, products and inerts which are liquid or gaseous under the conditions of reaction, wherein a catalyst system is arranged and supported in said reaction-distillation column, said method being characterised in that said catalyst system comprises a plurality of closed cloth pockets (32) containing a particulate catalytic material (33), the pockets being arranged and supported by wire mesh (31) intimately associated with said closed cloth pockets, said plurality of said pockets being contained in a single cloth belt, said cloth belt being coiled into a spiral and having said wire mesh disposed between coils of said cloth belt spiral.

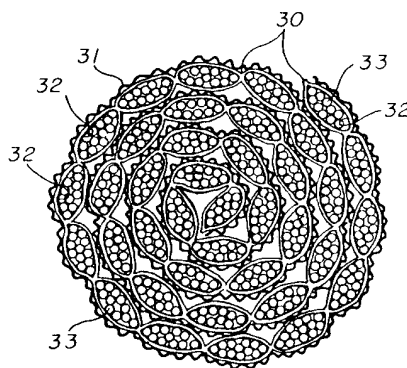


fig.3

CATALYTIC DISTILLATION

The present invention relates to conducting catalytic chemical reactions wherein separation of materials in the reaction mixture, i.e., product(s), by-product(s) or starting material(s) may be obtained by concurrent distillation or fractionation thereof.

In a specific application the present invention relates to the separation of isoolefins from streams containing mixtures of an isoolefin and the corresponding normal olefin. The present invention is especially useful for the separation of isobutene from streams containing n-butenes.

One species of the present invention relates to the preparation of methyl tertiary butyl ether from streams containing mixtures of an isobutene and normal C₄ olefin. The present invention is especially useful for the separation of isobutene from streams containing n-butenes.

Isoolefins of 4 carbon atoms are difficult to separate from the corresponding normal olefin by simple fractionation because of the closeness of their boiling points. In prior art processes as generally practiced commercially, the isoolefin is selectively absorbed by sulfuric acid and the resulting isoolefin-containing sulfuric acid extract is then diluted and heated or treated with steam to separate the isoolefin.

Isobutene and diisobutene are of significant value having diverse applications, for example, isobutene is one of the comonomers for butyl rubber and diisobutene is an intermediate in the preparation of detergents. The n-butenes are required in pure form for homopolymerization and as feeds for the oxidative production of butadiene. One manner of separating these components is to pass the mixture through what is called a cold acid extraction procedure wherein the stream is fed into a bath of concentrated sulfuric acid. Separation is achieved by virtue of the solubility of the isobutene in the sulfuric acid, the n-butenes and other hydrocarbons present passing overhead.

In an improved process reported in U.S. Pat. No. 3,531,539 to Tidwell, the C₄ feed stream containing isobutene was contacted with a molecular sieve at an elevated temperature and under sufficient pressure to maintain a liquid phase, wherein the isobutene is converted to diisobutene which is easily separated from the stream by conventional separation techniques.

Methyl tertiary butyl ether (MTBE) has gained a wide acceptance as a non environmentally harmful octane improver for gasolines. One method of separating isobutene or isoolefins in general from mixtures with the corresponding normal olefins and alkanes, has been to etherify the isoolefin with a C₁ to C₆ primary alcohol in the presence of an acidic cation exchange resin catalyst, separate the low boiling hydrocarbons from the higher boiling ether by fractionation, frequently followed by decomposition of the ether to recover the isoolefin. Such procedures are disclosed in U.S. Pat. No.'s 3,121,124; 3,270,081 and 3,170,000.

More recently, in view of the ether octane improving characteristics, similar processes have been disclosed for preparing and recovering the ether, e.g., U.S. Pat. No's 3,726,942 and 3,846,088.

In a variation on these processes disclosed in U.S. Pat. No.'s 3,629,478 and 3,634,534 to Haunschild, the mixture of isoolefin and normal olefin with lower primary alcohols is fed to distillation column in which there are a plurality of zones of acidic ion exchange resin catalyst whereby the isoolefin ether is formed and drops to the bottom of the column while the normal olefins (and paraffins) are distilled overhead. In particular, the catalyst is contained in downcomers where the reaction is to occur and the distillation takes place on the trays of the column.

US4039590 describes a fixed bed reaction of isobutene and methanol in a straight pass liquid phase system. An undesirable minor side reaction is mentioned which forms butenyl ethers. US2043672 discloses the use of an isomerization catalyst to isomerize butene-1 to butene-2 with the isobutene being fractionated. Dimerization is not part of this process.

German patent specification DE-PS 1075613 discloses a distillation column for performing organic chemical reactions in the presence of fine-grain catalysts. The fine-grain catalysts are located in wire baskets, which are arranged in the column in the manner of fillers. The wire baskets may be Raschig rings, whose top and bottom surfaces are closed by screens having a suitable mesh size. Fine-grain fillers may be located on the trays of a column, whose outlets are provided with sloping fine-mesh screens. There is no disclosure of a catalyst system as defined and utilised in the present invention (see below).

Chemiker-Zeitung/Chemische Apparatur, 90 Jg (1966), Nr. 13. pages 443-446 disclose catalytic reactions in ion exchange columns whilst displacing the chemical equilibrium. Those pages review advantages of fine exchange resins used in organic reactions. There is no disclosure of a catalyst system as defined and utilised in the present invention (see below).

The method of the present invention may be used for carrying out chemical reactions wherein the materials of the reaction mixture are separated by distillation. The method may be used with reactants,

products and inerts which are liquid or gaseous under the conditions of the reaction. The reactants may be a single material, such as isobutylene which reacts with itself to form diisobutylene in a C₄ stream containing normal butenes, wherein the normal butenes are recovered as an overhead and the diisobutylene recovered as bottoms or the reactants may be different materials such as isobutene and methanol described in more detail herein. It is the discovery of the use of the catalyst system as both the catalyst and the distillation packing such that reaction and distillation are occurring concurrently in the fixed catalyst bed, which is the basis of the present invention.

The present invention includes the separation of isoolefins, preferably having four to six carbon atoms, from streams containing mixtures thereof with the corresponding normal olefins. For example, streams containing isobutene and normal butene, isopentene and normal pentene and isohexene and normal hexene.

The present invention provides a method of carrying out chemical reactions in a reaction-distillation column, wherein the materials of a reaction mixture are separated by distillation, the method being used with reactants, products and inerts which are liquid or gaseous under the conditions of reaction, wherein a catalyst system is arranged and supported in said reaction-distillation column, said method being characterised in that said catalyst system comprises a plurality of closed cloth pockets (32) containing a particulate catalytic material (33), the pockets being arranged and supported by wire mesh (31) intimately associated with said closed cloth pockets, said plurality of said pockets being contained in a single cloth belt, said cloth belt being coiled into a spiral and having said wire mesh disposed between coils of said cloth belt spiral."

Said method of the present invention may be characterised in example by being a method of preparing methyl-tertiary-butyl-ether by contacting a mixture containing isobutene and n-butene with methanol in a fixed bed acid cation exchange resin packing whereby catalytically reacting the isobutene with methanol followed by fractionating the resulting mixture, wherein the mixture and methanol are concurrently contacted with the acid cation exchanged resin in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation-reaction zone, followed by concurrently withdrawing the ether obtained from the distillation column reactor at a point below the feed zone of the mixture and methanol and withdrawing the normal butene at a point above the feed zone of the mixture and the methanol.

Said method of the present invention may be characterised in example by being a method of preparing isobutene by contacting methyl-tertiary-butyl-ether with a fixed bed acid cation exchange resin packing thereby catalytically dissociating the methyl-tertiary-butyl-ether into methanol and isobutene, wherein the methyl-tertiary-butyl-ether is contacted with the fixed bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation dissociation zone, followed by continuously withdrawing the isobutene from the distillation column reactor at a point above the feed zone of the methyl-tertiary-butyl-ether and methanol at a point below said feed zone.

Said method of the present invention may be characterised in example by being a method of producing diisobutene by contacting methyl-tertiary-butyl-ether with a fixed bed acid cation exchange resin packing thereby catalytically dissociating the methyl-tertiary-butyl-ether into methanol and diisobutene, wherein the methyl-tertiary-butyl-ether is contacted with the fixed bed cation exchange resin packing, in a distillation column reactor the acid cation exchange resin beads being placed into into a plurality of pockets in a cloth belt is the distillation dissociation zone, followed by continuously withdrawing diisobutene and methanol from the distillation column reactor at a point below the feed zone of the methyl-tertiary-butyl-ether .

Said method of the present invention may be characterised in example by being a method of preparing diisobutene contacting a C₄ hydrocarbon stream containing isobutene with a fixed bed acid cation exchange resin packing thereby catalytically reacting isobutene with itself to form diisobutene, wherein the stream is contacted with a fixed bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation zone, followed by continuously withdrawing at a point above the feed zone of the C₄ hydrocarbon stream containing isobutene and said diisobutene is withdrawn at a point below said feed zone.

Said method of the present invention may be characterised in example by being a method for separating isoolefins from a mixture containing isoolefins and normal olefin by contacting the mixture with a fixed bed acid cation exchange resin packing thereby catalytically reacting isoolefin with itself to form a dimer, wherein the mixture is contacted with the fixed bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation zone while the resulting mixture of normal olefins and dimer is fractionated, and said dimer is withdrawn from said distillation column reactor at a point below the feed zone of the mixture containing isoolefin and normal olefin.

The catalyst-packing material is a central feature of the invention, clearly without it the process as described can not be carried out. The shaped catalyst which is employed may also be employed in other processes, such as liquid phase contact with aqueous or organic systems to carry out procedures known in the art, and which may be carried out with catalyst in the prior art in other forms such as beads, pellets or
 5 the like. It should be appreciated that the distillation functional catalyst compositions of the present invention provide a more open packing as is required for distillation, hence if the present catalyst-packing is employed in a liquid phase process, a larger bed will be required to obtain the comparable degree of liquid-catalyst contact as compared for example to close packed solid beds of small beads.

The particular shape of the catalytic material is not critical, so long as the shape functions as a
 10 distillation packing. Thus, balls, chunks, sheets, tubes or spirals of catalytic material may be employed as well as the conventional distillation shapes noted above.

The catalytic material may be any material appropriate for the reaction at hand, that is, it may be an acid catalyst or a basic catalyst or others such as catalytic metals and their oxides or halides suitable for a multitude of catalytic reactions and of course, the catalyst is heterogeneous with the reactants or other
 15 fluids in the system.

For example, a different reaction is the preparation of formic acid from methanol using iron oxide or transesterification using a base catalyst such as NaOAl.

The term "catalyst" or "catalytic material" is used to include any solid material which is recognized for the reaction under consideration as performing as a catalyst therein.

Thus, the catalytic material is more than that in the present invention. It is a distillation part or component since it is also the distillation packing (note there may be inert distillation packing in the column also, such as, below or above the catalytic packing, between beds of catalytic packing or intermixed into the catalytic packing). Thus, broadly stated, the catalytic material is a component of a distillation system
 20 functioning as both a catalyst and a distillation packing, i.e., a packing for a distillation column having both a distillation function and a catalytic function.

It has been found that the resin beads in a conventional fixed bed form too compact a mass for the upward flowing vapor and downward flowing liquid. However, it has been found that by placing the resin beads into a plurality of pockets in a cloth belt, which is supported in the distillation column reactor by open mesh knitted stainless steel wire by twisting the two together, allows the requisite flows, prevents loss of
 30 catalyst, allows for the normal swelling of the beads and prevents the breakage of the beads through mechanical attrition. This novel catalyst arrangement is also part of the present invention.

The cloth may be of any material which is not attacked by the hydrocarbon feed or products under the conditions of the reaction. Cotton or linen may be used, however, fiber glass or "teflon" cloth are preferred. Briefly, a preferred catalyst system comprises a plurality of closed cloth pockets containing particulate catalytic material arranged and supported in said distillation column reactor by wire mesh intimately
 35 associated therewith.

The particulate catalytic material may be a powder, small irregular fragments or chunks, small beads and the like. The particular form of the catalytic material in the cloth pockets is not critical, so long as sufficient surface area is provided to allow a reasonable reaction rate. This sizing of catalyst particles can be best determined for each catalytic material (since the porosity or available internal surface area will vary for different materials and of course affects the activity of the catalytic material).
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What readily distinguishes the present method from prior art is that the prior art has consistently employed a continuous liquid phase system for contacting the isoolefin with the acidic catalyst, whereas the present invention carries out the method in a catalyst packed distillation column which can be appreciated
 45 to contain a vapor phase and some liquid phase as in any distillation. The dimerization reaction of isobutene and the fractionation of the resultant n-butene-dimer mixture is carried out simultaneously, i.e., concurrently. That is as the dimer is formed in the catalyst bed, the lower boiling n-butene is fractionated away in the catalyst bed and removed overhead while the high boiling dimer drops to the lower portion of the column.

The bulk type liquid phase reactions of the prior art had as one problem the control of the temperature. The distillation avoids this problem entirely.
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Thus, the catalyst packing is of such a nature as to allow the vapor flow through the bed, yet provide a sufficient surface area for catalytic contact. In the process described in the earlier mentioned Haunschild patents, the catalyst is packed into the downcomers and maintained in what is a flooded state as the
 55 liquid in the column passes down through the downcomer to the next lower tray. The material from the downcomer is then fractionated on the lower tray as in a conventional tower.

For example, according to the present invention a higher boiling reactant is continually contacted with the catalyst and lower boiling reactants passing upward in the fixed catalyst bed which provides more

opportunity for reaction. Similarly, the removal of a reaction component from the reaction mixture of a reversible reaction, forces the reaction to completion. Thus, in procedures where catalytic reaction and fractionation are features, the present process provides both functions in a single step. The equipment is very simple, and can utilize any type of distillation tower (provided the fixed beds of catalyst can be inserted therein to fill the reaction-distillation zone). It can be appreciated that any packing will restrict the vapor flow in the column and that if alternate unpacked avenues of travel are provided, the vapor will follow the route of least resistance. Thus, in a reactor configuration such as shown in the Haunschild patents, no vapor contact or flow could or would proceed through the catalyst packed downcomers.

The present process is also useful for reacting one material in a multicomponent feed and concurrently separating unreacted components of the feed therefrom by fractionation.

The fractionation may be directed to recovering a product overhead or as a bottom fraction. It may also be directed to recovering a non reactant such as n-butene from the reaction mixture of isobutene and methanol, the n-butene being a feed stream component which is otherwise difficult to separate from the isobutene. Thus, the present disclosed process may be used for specific reactions between relatively pure reactants or the selective reaction and recovery of desired products from mixed feeds.

It is to be expected that for any particular feed stream and selective reaction therein, the specific conditions of reaction will need to be determined by some minimum amount of experimentation employing the invention as described herein and using information provided herein to conduct the process in accordance with the present invention. Similarly, although the illustrations are primarily directed to mixed C₄ streams wherein isobutene is selectively reacted, other streams and processes are contemplated, as for example, isomerizations of butene-2 to butene-1 and the concurrent fractionation of the resulting isomerization mixture. Furthermore, in addition to dimerization, etherification and isomerization, all other types of reactions are contemplated within the scope of the process, for example, esterification, chlorination, hydration, dehydrohalogenation, alkylation, polymerization, and the like.

The reactants (and inerts) are generally organic compounds (although some inorganic compounds may be dissolved therein). Although C₄ hydrocarbons are illustrated, it is contemplated that organic compounds which are fluid and produce reaction products which are fluid under the conditions of operation and which are subjected to fractionation for separation or recovery of materials from the reaction are all suitable for use in the present process.

Thus, in its generic form, the present invention enables concurrently conducting chemical reactions to produce a reaction mixture and fractionation of the reaction mixture comprising:

(a) feeding reactants to a distillation column reactor into a feed zone,

(b) concurrently:

(1) contacting said reactants with a fixed bed catalyst packing in a form which provides distillation sites in a distillation-reaction zone, thereby catalytically reacting said reactants to form a reaction mixture,

(2) fractionating the resulting reaction mixture in said fixed bed catalyst to recover a lower boiling fraction of said reaction mixture overhead and a higher boiling fraction thereof as a bottom, whereby said reaction and fractionation are occurring concurrently within the fixed catalyst bed which serves as both catalyst and distillation packing in said distillation column reactor.

Furthermore, the catalytic material must be in a form to serve as a distillation packing, for example rings, saddles, balls, irregular pieces, sheets, tubes, spirals, packed in bags.

Broadly stated, the catalytic material is a component of a distillation system functioning as both a catalyst and distillation packing, i.e., a packing for a distillation column having both a distillation function and a catalytic function.

One species of the present invention is a method for the preparation of methyl tertiary butyl ether from streams containing mixtures of isobutene and normal butene.

The use of the invention for producing methyl tertiary ether comprises (a) feeding a mixture containing an isobutene and normal butene to a distillation column reactor into a feed zone, (b) feeding methanol into said feed zone (c) concurrently: (1) contacting said mixture and methanol with a fixed bed acidic cation exchange resin packing in a distillation-reaction zone, thereby catalytically reacting the isobutene with methanol to form methyl tertiary butyl ether, and (2) fractionating the resulting mixture of ether and normal olefin, (d) withdrawing the ether from the distillation column reactor at a point below said feed zone and (e) withdrawing the normal olefin from the distillation column reactor at a point above the feed zone, preferably above the acidic cation exchange resin.

A particular embodiment of the present invention is for the separation of isobutene from a mixture comprising n-butene and isobutene. More generally, the invention is suitable for the separation of isobutene from a hydrocarbon stream which is substantially C₄ hydrocarbons, such as n-butane, isobutene, n-butene, isobutane, and butadiene (minor amounts of C₃ and C₅ hydrocarbons, i.e., less than 10% may be

incidental components of such C₄ stream).

Briefly stated, separating isobutene comprises:

(a) feeding a mixture containing isobutene and n-butene and methanol to a distillation column reactor into a feed zone,

(b) concurrently:

(1) contacting said mixture and methanol with a fixed bed acidic cation exchange resin packing in a distillation-reaction zone, thereby catalytically reacting isobutene with methanol to form methyl tertiary butyl ether, and

(2) fractionating the resulting mixture comprising methyl tertiary butyl ether and n-butene,

(c) withdrawing said methyl tertiary butyl ether from said distillation column reactor at a point below said feed zone and,

(d) withdrawing n-butene from said distillation column reactor at a point above the feed zone.

The reaction system can be described as heterogeneous since the catalyst remains as a distinct entity. The catalyst may be employed in such conventional distillation packing shapes, as Raschig rings, Pall rings, saddles or the like. Similarly, the resin may be employed in a granular or bead form as described herein.

The methanol may be and is preferably present in a stoichiometric amount although an excess of up to 10%, may be desirable. In addition, slightly less than a stoichiometric amount may be employed. It should be appreciated that the skilled chemist will optimize the proportions and precise conditions for each particular piece of equipment and variation in catalyst, once the basic invention is comprehended.

It has been found that the resin beads in a conventional fixed bed form too compact a mass for the upward flowing vapor and downward flowing liquid. However, it has been found that placing the resin beads into a plurality of pockets in a cloth belt, which is supported in the distillation column reactor by open mesh knitted stainless steel wire by twisting the two together, allows the requisite flows, prevents loss of catalyst, allows for the normal swelling of the beads and prevents the breakage of the beads through mechanical attrition. This novel catalyst arrangement is described herein.

The etherification reaction of isobutene and the fractionation of the resultant n-butene-ether mixture is carried out simultaneously, i.e., concurrently. That is as the ether is formed in the catalyst bed the lower boiling n-butene is fractionated away in the catalyst bed and removed overhead while the high boiling ether drops to the lower portion of the column.

The bulk type liquid phase reactions of the prior art had as one problem the control of the temperature. The distillation avoids this problem entirely.

The Hauschild patents described above, were an improvement in that there was some etherification catalyst in the column but the etherification and distillation were not concurrent. Etherification occurs only in the liquid phase in the downcomers with distillation occurring subsequently on the tray, thus teaching only a contact with the catalyst in the down flow of the reactants severely limited the reaction and prompted the patentee to suggest multiple conventional fixed bed reactions of isobutene and alcohol to form ether prior to introduction to various trays in the distillation column.

Another species of reaction, which is closely related to the MTBE production is the production of high purity isobutene from the dissociation of MTBE. This reaction is obtained by feeding MTBE to the catalyst bed packing in the reaction-distillation column, recovering methanol bottoms and high purity (95% +) isobutene overhead product, using the same acidic resin catalyst. The feed zone is the upper end of the catalyst bed.

In another closely related species of reaction, the reaction of methanol and isobutene is conducted as described herein, generally, but the amount of methanol is less than stoichiometric amount. By raising temperatures (e.g., increase the pressure in the column) and the dimerization of isobutene is favored. A bottoms product of high purity diisobutene (fewer codimers than in the usual type of process to produce diisobutene from C₄ streams) is obtained.

The present invention will be further described, by way of example only, with reference to the accompanying drawings, in which :-

Fig.1 is a schematic representation of a catalytic distillation column for use in this invention.

Fig.2 is an elevational view of a catalyst belt packing.

Fig.3 is a cross sectional view of the catalyst belt packing taken along 3-3 of Fig.2.

Mixed C₄ streams containing principally isobutane (I-C₄), normal butane (n-C₄), butene-1 (B-1), isobutene (I-B), trans butene-2 (TB-2) and cis butene-2 (CB-2) (plus some minor impurities including butadiene), can be treated with cold sulfuric acid to remove isobutene and produce a butylene concentrate. The isobutene removed is recovered from the acid as a polymer (mostly dimer). The isobutene dimer (i.e., some other isobutene polymers as well) and butene concentrate are valuable products.

A substitute route for accomplishing this same separation has been discovered. It has been found that a distillation column packed with a properly supported acid catalyst can produce a bottom stream containing isobutene polymer (most dimer) and an overhead stream that is relatively free of isobutene. This is surprising since the catalyst used would normally produce mostly heavy isobutene polymers and copolymers if the reaction were conducted in a conventional fixed bed.

It has been found that a distillation column packed with a properly supported acid catalyst into which the mixed C₄ stream and methanol are fed can produce a bottom stream containing methyl tertiary butyl ether and an overhead stream that is relatively free of isobutene.

The success of the catalytic distillation approach lies in an understanding of the principles associated with distillation. First, because the reaction is occurring concurrently with distillation, the initial reaction product, e.g., methyl tertiary butyl ether (or diisobutylene) is removed from the reaction zone nearly as quickly as it is formed. This removal of the ether (or isobutene dimer) minimized decomposition of the ether and chaining to form isobutene polymer (or further chaining to large polymer lengths is in the case of dimerization). Second, because all the C₄ components are boiling, the temperature of the reaction is controlled by the boiling point of the C₄ mixture at the system pressure. The heat of reaction simply creates more boil up, but no increase in temperature. Third, the reaction has an increased driving force because the reaction products have been removed and can not contribute to a reverse reaction (LeChatelier's Principle).

As a result, a great deal of control over the rate of reaction and distribution of products can be achieved by regulating the system pressure. Also, adjusting the through-put (residence time = liquid hourly space velocity⁻¹) gives further control of product distribution and degree of isobutene removal.

The temperature in the reactor is determined by the boiling point of the C₄'s at any given pressure, that is, at constant pressure a change in the temperature of the system, indicates a change in the composition in the column. Thus, to change the temperature the pressure is changed. By increasing the pressure, the temperature in the system is increased. Generally, pressures in the range of 0 to 400 psig (1 to 28.59 bar) are or may be employed, preferably 30 to 150 psig (13.08 to 11.35 bar). For the C₄ stream, the present reaction will be carried out generally at pressures in the range of 10 to 300 psig (1.70 to 21.70 bar), which will generally mean temperatures in the range of 10 to 100 °C.

The reaction of isobutene with itself is equilibrium limited; however, by carrying out the reaction in a distillation column reactor and fractionating the formed product (diisobutene) downward away from the reaction zone, the equilibrium is constantly disrupted and hence the reaction never comes to equilibrium. This has the advantage of course, of achieving an effective 100% conversion (provided the catalyst bed is of sufficient length such that none of the isobutene escapes therefrom to go overhead with the n-butenes). The adjustment of the size of the catalyst bed is a mere mechanical step to be determined for each reactor and in accordance with the reaction conditions.

The system would normally be considered anhydrous; however, small amounts of water often saturate the feed stream and represent about 400 to 600 ppm thereof. The process will continue to operate in the same fashion, in the presence of this amount of water; however, the following effects have been observed: (1) all of the rates increase, however, the lower rates increase faster. (Although not mentioned above, those in the art will recognize that there is a reaction of isobutene with butene to produce "codimer". This rate is normally much slower than the diisobutene rate). (2) the amount of codimer increases and (3) tertiary butanol is produced in small amounts.

The feed to the distillation column reactor is made at the lower end of the catalyst bed, preferably into the catalyst to allow immediate contact of the isobutene with the catalyst.

The reaction of isobutene with methanol is equilibrium limited; however, by carrying out the reaction in a distillation column reactor and fractionating the formed product, methyl tertiary butyl ether (MTBE), downward away from the reaction zone, the equilibrium is constantly disrupted and hence the reaction never comes to equilibrium. This has the advantage of course, of achieving an effective 100% conversion, provided the catalyst bed is of sufficient length such that none of the isobutene escapes therefrom to go overhead with the n-butenes (a problem the Hauschild process does not solve). The adjustment of the size of the catalyst bed is a mere mechanical step to be determined for each reactor and in accordance with the reaction conditions.

The MTBE system would normally be considered anhydrous; however, small amounts of water often saturate the feed stream and represent about 400 to 600 ppm thereof. The process will continue to operate in the same fashion, in the presence of this amount of water. Generally the system will be employed with less than 1 mole % water in the feed. However, the limitation on water is relevant to the MTBE reaction. Quite obviously, where water is a reactant or a principal component of a feed stream according to the generic invention, it may be present in substantially larger amounts as required,

The feed of the distillation column reactor is made at the lower end of the catalyst bed for the MTBE

reaction, preferably into the catalyst to allow immediate contact of the isobutene and methanol with the catalyst which is characterized as the feed zone.

A reflux is preferably included in the system. The reflux ratio could vary over the rate of 1 to 20:1. In practice, the higher ratio may be used to compensate for a short catalyst bed such as required for experimental work. In commercial size units the catalyst bed would be provided so that lower reflux and hence higher unit productivity could be obtained.

The cation resins are those which have been used in the prior art for this reaction. Catalysts suitable for the new MTBE process are cation exchanger, which contain sulfonic acid groups, and which have been obtained by polymerization or copolymerization of aromatic vinyl compounds followed by sulfonation. Examples of aromatic vinyl compounds suitable for preparing polymers or copolymers are: styrene, vinyl toluene, vinyl naphthalene, vinyl ethylbenzene, methyl styrene, vinyl chlorobenzene and vinyl xylene. A large variety of methods may be used for preparing these polymers; for example, polymerization alone or in admixture with other monovinyl compounds, or by crosslinking with polyvinyl compounds; for example, with divinyl benzene, divinyl toluene, divinylphenylether and others. The polymers may be prepared in the presence or absence of solvents or dispersing agents, and various polymerization initiators may be used, e.g., inorganic or organic peroxides, persulfates, etc.

The sulfonic acid group may be introduced into these vinyl aromatic polymers by various known methods; for example, by sulfating the polymers with concentrated sulfuric acid or chlorosulfonic acid, or by copolymerizing aromatic compounds which contain sulfonic acid groups (see e.g., U.S. Pat. No. 2,366,007). Further, sulfonic acid groups may be introduced into these polymers which already contain sulfonic acid groups; for example, by treatment with fuming sulfuric acid, i.e., sulfuric acid which contains sulfur trioxide. The treatment with fuming sulfuric acid is preferably carried out at 0 to 150°C, and the sulfuric acid should contain sufficient sulfur trioxide after the reaction. The resulting products preferably contain an average of 1.3 to 1.8 sulfonic acid groups per aromatic nucleus. Particularly, suitable polymers which contain sulfonic acid groups are copolymers of aromatic monovinyl compounds with aromatic polyvinyl compounds, particularly, divinyl compounds, in which the polyvinyl benzene content is preferably 1 to 20% by weight of the copolymer (see, for example, German Patent Specification 908,247).

The ion exchange resin is preferably used in a granular size of about 0.25 to 1 mm, although particles from 0.15 mm up to about 1 mm may be employed. The finer catalysts provide high surface area, but also result in high pressure drops through the reactor. The macroreticular form of these catalysts is preferred because of the much larger surface area exposed and the limited swelling which all of these resins undergo in a non-aqueous hydrocarbon medium.

Similarly, other acid resins are suitable, such as perfluorosulfonic acid resins which are copolymers of sulfonyl fluorovinyl ethyl and fluorocarbon and described in greater detail in DuPont "Innovation", Volume 4, No. 3, Spring 1973 or the modified forms thereof as described in U.S. Pat. No.'s 3,784,399; 3,770,567 and 3,849,243.

Fig. 1 illustrates schematically a typical distillation column in which the present process may be carried out. The column 10 was a one inch (25.4 mm) diameter, five foot (1.54 m) tall tube containing two feet (0.60 m) of conventional glass 1/6 inch (1.6 mm) helices 18 and three feet (0.91 m) of the catalytic packing as shown in Figs. 2 and 3.

Fig. 2 shows a cloth belt 30 wrapped in open mesh knitted stainless steel wire 31. The cloth bag 30 is composed of a plurality of vertical pockets 32 sewn into the bag. Each pocket 32 is filled with resin catalyst 33.

The wire mesh provides the support for the catalyst (belt) and provides some degree of vapor passage through the catalyst beads, which otherwise form a very compact bed which has a high pressure drop. Thus, the down flowing liquid is in intimate contact with the rising vapors in the column.

In commercial-scale operations, it is contemplated, catalyst packing would be made up of alternating layers of resin-filled cloth belts similar to the ones described above, and a spacing material which could be of any convenient, suitable substance, such as a corrugated wire screen or wire cloth or a knitted wire mesh. The layers would be arranged vertically to provide vapor passages between the belts. The cylindrical resin-filled pockets could be oriented either vertically or horizontally. For simplicity of fabrication and for better distribution of vapor flow passages, a vertical orientation is preferred. The height of a section of this packing could be of any convenient dimension, from a few inches (mm) to several feet (m). For each of assembly and installation, the packing would be made into sections of the desired shape and size, each section fastened together with circumferential bands or tie wires depending on its size and shape. A complete assembly in a column would consist of several sections, arranged in layers, with the orientation of the resin-filled belts turned at right angles in successive layers to improve liquid and vapor flow distribution.

Other configurations which may be useful but with certain draw backs would be cages of wire cloth to contain catalyst beads, immersed in liquid on a conventional sieve tray. Disadvantages would be the restriction of vapor flow by the close weave of the wire, which may be compensated by allowing the beads to move freely in the cage, thereby causing attrition. Similarly, suspension of the catalyst on a tray would present problems of attrition, maintaining suspension and preventing catalyst from leaving the tray.

In the laboratory column the bags are made in the form of a cloth belt approximately six inches (152 mm) wide with narrow pockets approximately $\frac{3}{4}$ inch (19 mm) wide sewn across the belt. The pockets are spaced about $\frac{1}{8}$ inch (3.8 mm) apart. These pockets are filled with the catalyst beads to form approximately cylindrical containers, and the open ends are then sewn closed to confine the beads. This belt is then twisted into a helical form to fit inside the one inch (25.4 mm) column. Twisted in with the belt is also a strip of an open mesh knitted stainless steel wire, which serves to separate the resin filled cloth pockets and provide a passage for vapor flow.

In operation, during the dimerization, the isobutene containing C_4 feed enters through line 11 into the lower end of the catalytic zone 24 which contains the catalyst bag belt 25 as described. The temperature and pressure in the column are such that the C_4 boils up in the column, however, as the isobutene contacts the catalyst, dimer is formed, which being higher boiling than the C_4 stream, passes to the bottom of the reactor where it is removed via line 20 with a portion being recovered through line 21 and another portion recycled into reboiler 19 through line 22 and hence back into the bottom of the column 10 through line 23.

Meanwhile, the n-butenes pass upward through the catalyst zone 24 and out of the column 10 via line 12 to condenser 13 hence into accumulator 15 via line 14. A portion is recovered as butene concentrate from line 16 and a portion is returned as reflux through line 17 into column 10.

EXAMPLES

In the following examples *, the feed rate of C_4 's to the column is adjusted to maintain a bottoms temperature which would correspond to low C_4 concentration. The catalyst employed was Amberlyst 15, manufactured by Rohm and Haas, Philadelphia Pa. The C_4 feed had the following composition:

Component	mole %
Isobutane	2.8
n-Butane	8.6
Butene-1	24.6
Isobutene	50.5
Trans-butene-2	10.4
Cis-butene-2	3.1
Butadiene	.5
ratio butene-1/butene-2	1.8

The laboratory distillation-reactor column was a one inch (25.4 mm) diameter, five foot (1.54 m) tall tube containing two feet (0.60 m) of conventional glass 1/16 inch (3.2 mm) helices and three feet (0.914 m) of the catalytic packing. The pilot column is 3 inches (76.2 mm) in diameter with 10 feet (3.04 m) of catalyst packing and 5 feet (1.52 m) of conventional $\frac{3}{8}$ inch (9.5 mm) pall rings.

In operation, the isobutene containing C_4 feed and methanol enters into the lower end of the catalytic zone which contains the catalyst bag belt as described. The temperature and pressure in the column are such that the C_4 and methanol boil up in the column, however, as the isobutene and alcohol contact the catalyst, ether is formed, which being higher boiling than the C_4 stream, passes to the bottom of the reactor where it is removed. Generally a portion is recovered through and another portion recycled into a reboiler and hence back into the bottom of the column.

Meanwhile, the n-butenes pass upward through the catalyst zone and out of the column to a condenser hence into an accumulator. In normal operation, a portion is recovered as butene concentrate and a portion is returned as reflux through into the column.

Examples 1, 2, 3, 9 and 10.

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EXAMPLES 1, 2 and 3

These runs illustrate MTBE production.

Example	<u>1</u>	<u>2</u>	<u>3</u>
	<u>Laboratory Column</u>		<u>Pilot Plant Column</u>
	LHSV ^{*-1} = 1.0 hr		LHSV ⁻¹ = 1.4 hr
	115 g (190 ml) cat		2640 g (4400 ml) cat
System pressure	80 psig (6.5 bar)		100 psig (7.9 bar)
Temperature:			
Bottoms	228 ° F (109 ° C)		260 ° F (127 ° C)
Middle cat. bed	138 ° F (59 ° C)		160 ° F (71 ° C)
Methanol Feed	2.5 ml/min		24 ml/min
Reactor Recovery Rate			
Overhead, grams/hr	120	---	3060 ml/hr
Bottoms, grams/hr	264	---	4980 ml/hr
Analysis, Mole % Overhead			
Isobutane	6.1	6.6	6.1
Normal butane	18.0	15.5	15.8
Butene-1	40.6	40.5	47.0
Isobutene	11.2	9.8	1.3
Trans-butene-2	18.8	19.1	24.2
Cis-butene-2	5.1	5.2	5.2
Butadiene	.3	.3	.3
Bottoms			
Methanol and C ₄ 's	5.5	7.8	1.3
Tertiary Butyl alcohol	2.5	.7	.7
Methyl tertiary butyl ethyl (MTBE)	93.2	91.2	91.9
C ₈ 's and heavier	.8	.3	6.1
The process operated according to the present invention gives excellent yields of MTBE at a reasonable feed rate.			

* LHSV⁻¹ calculated by dividing overhead take-off rate into the volume of resin in the catalytic zone.

Examples 4 and 5

These examples illustrate the production of high purity isobutene from methyl tertiary butyl ether. The one inch laboratory column was used and packed with 72 grams of catalyst distillation packing as described in pockets of a cloth belt. The catalyst was in the lower portion of the column for this reaction and the feed (MTBE) was at the upper end of the catalyst bed. Two runs were made using two different purities of feed.

The conditions and results are set out below:

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Example	4	5
Feed Mole % MTBE	95.6%	99.1%
Recovery Rate		
Overhead ml/hr	100	100
Bottom	not recorded	not recorded
Pressure, psig	70 (5.84 bar)	80 (6.53 bar)
Temperature, °F		
Overhead	118 (48 °C)	122 (50 °C)
Bottoms	212 (100 °C)	220 (104 °C)
Middle cat. bed	214 (101 °C)	217 (103 °C)
Analysis, %*		
Overhead		
Isobutane	.02	.05
Nornal butane	.4	.01
Butene-1	.5	.05
Isobutene	96.5	99.6
Trans-butene-2	1.6	.2
Cis-butene-2	.9	1.2
Butadiene	.03	.01
Bottom	mixture of MTBE and methanol	mixture of MTBE and methanol

* gas phase chromatography area

Examples 6, 7 and 8

Example 6 illustrates the flexibility of the present process to produce high purity diisobutene from the reaction of methanol and isobutene or MTBE only. The three inch (76.2 mm) pilot column was used. In Example 7 the column was modified by adding an additional 5 feet (1.54 m) of column. In Example 6, the column contained 5 feet (1.54 m) of conventional Pall ring in the lower portion and 10 feet (3.08 m) of the catalyst in cloth bags in the upper portion. In Example 7, an additional 2.5 feet (0.76 m) of catalyst packing was added and 2.5 feet (0.76 m) of $\frac{1}{4}$ inch (6.3 mm) conventional saddles on top of that. In both runs, methanol was fed at the top of the catalyst bed and the C₄ feed (as described above) was fed below the catalyst bed. The feed rates were adjusted to obtain the desired product distribution.

In Example 8, high purity methyl tertiary butyl ether (99%) was the feed to column as employed in Example 7. The MTBE was fed into the column at the bottom of the catalyst bed. There was essentially no overhead removed except that necessary for analysis. The example demonstrates a unique method for producing diisobutene having a very low codimer contamination. The condition and results of the runs are described below:

Example	6**	7	8
<u>Rate of Recovery</u>			
Overhead, liters/hr	4.5	3.0	essentially 0
Bottoms, liters/hr	4.5	4.2	4.5
<u>Pressure, psig</u>	100 (7.91 bar)	120 (9.29 bar)	78 (6.39 bar)
<u>Temperature °F</u>			
Overhead	155 (68°C)	158 (70°C)	82 (28°C)
Bottoms	350 (177°C)	260 (127°C)	245 (118°C)
Middle Cat. bed	180 (52°C)	165 (74°C)	220 (104°C)
<u>Analysis %*</u>			
<u>Overhead</u>			
Isobutane	6.5	6.2	-
Normal butane	17.0	17.0	1.5
Butene-1	32.2	46.9	.8
Isobutene	6.2	trace	69.6
Trans-butene-2	28.5	24.2	.4
Cis butene-2	9.4	5.0	-
Butadiene	.2	.6	-
Dimethyl ether			27.7
<u>Bottoms</u>			
Lights, methanol	.3	3.2	.6
Tertiary butyl alcohol		1.0	5.1
MTBE	32.9	95.6	68.7
Unknown ether	2.2		.1
Diisobutene			
2,4,4-Trimethyl pentene-1	40.2		17.6
2,4,4-Trimethyl pentene-2	10.5		5.3
Codimers	7.1		.1
Back flush heavies	7.0	.2	2.4
Triisobutene			

* gas phase chromatography area

**reduced methanol below stoichiometric amount

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Example 9		
System Pressure = 70psig (5.84 bar)		
Catalytic zone temperature = 60 ° C		
Results:		
OVERHEAD:		
Component	Mole % component at LHSV ⁻¹ (Hrs)*	
	0.2	0.7
isobutane	5.8	4.6
n-butane	20.0	28.7
butene-1	31.6	15.6
isobutene	7.4	1.5
trans-butene-2	26.7	37.7
cis-butene-2	8.4	11.9
butadiene	.18	.03
ratio butene-1/butene-2	1.2	.3
Overhead take-off (ml/hr)	480	160
bottom temp ° C	133	171
bottom C ₄ 's (mole %)	9.8	2.7
BOTTOM:**		
component		
tert-butyl alcohol	.14	.04
diisobutene	61.6	51.5
codimer	18.0	31.3
triisobutene	16.8	12.9
heavies	3.5	4.2

* LHSV⁻¹ is calculated by dividing the overhead take-off rate into the volume of resin in the catalytic zone. (The zone contained 115 grams (190 ml) of catalyst).

** C₄'s are normalized out

Example 10		
System Pressure = 40 psig (3.77 bar)		
Catalytic zone temperature = 40 ° C		
Results:		
<u>OVERHEAD:</u>		
Component	mole % component at LHSV ⁻¹ (Hrs)*	
	0.7	1.4
isobutane	4.8	5.7
n-butane	15.1	16.0
butene-1	44.3	43.8
isobutene	12.1	9.3
trans-butene-2	18.6	20.0
cis-butene-2	4.8	5.1
butadiene	.21	.2
ratio butene-1/butene-2	1.9	1.7
Overhead take-off (ml/hr)	160	80
bottom temp ° C	142	159
bottom C ₄ 's (mole %)	3.0	.4
<u>BOTTOM:**</u>		
Component		
tert-butyl alcohol	.26	.11
diisobutene	75.0	74.5
codimer	10.2	12.6
triisobutene	11.6	10.2
heavies	2.9	2.6

* LHSV⁻¹ is calculated by dividing the overhead take-off rate into the volume of resin in the catalytic zone. (The zone contained 115 grams (190 ml) of catalyst).

** C₄'s are normalized out.

Claims

1. A method of carrying out chemical reactions in a reaction-distillation column, wherein the materials of a reaction mixture are separated by distillation, the method being used with reactants, products and inerts which are liquid or gaseous under the conditions of reaction, wherein a catalyst system is arranged and supported in said reaction-distillation column, said method being characterised in that said catalyst system comprises a plurality of closed cloth pockets (32) containing a particulate catalytic material (33), the pockets being arranged and supported by wire mesh (31) intimately associated with said closed cloth pockets, said plurality of said pockets being contained in a single cloth belt, said cloth belt being coiled into a spiral and having said wire mesh disposed between coils of said cloth belt spiral.

2. A method as claimed in claim 1, characterised by being a method of preparing methyl-tertiary-butyl-ether by contacting a mixture containing isobutene and n-butene with methanol in a fixed bed acid cation exchange resin packing thereby catalytically reacting the isobutene with methanol followed by fractionating the resulting mixture, wherein the mixture and methanol are concurrently contacted with the acid cation exchange resin in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation-reaction zone, followed by concurrently withdrawing the ether obtained from the distillation column reactor at a point below the feed zone of the mixture and the methanol and withdrawing the normal butene at a point above the feed zone of the mixture and the methanol.

3. A method as claimed in claim 1, characterised by being a method of preparing isobutene by contacting methyl- tertiary-butyl-ether with a fixed bed acid cation exchange resin packing thereby catalytically dissociating the methyl-tertiary-butyl-ether into methanol and isobutene, wherein the methyl-tertiary-butyl-

ether is contacted with the fixed bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation dissociation zone, followed by continuously withdrawing the isobutene from the distillation column reactor at a point above the feed zone of the methyl-tertiary-butyl-ether and methanol at a point below said feed zone.

5 4. A method as claimed in claim 1, characterised by being a method of producing diisobutene by contacting methyl- tertiary-butyl-ether with a fixed bed acid cation exchange resin packing thereby catalytically dissociating the methyl-tertiary-butyl-ether into methanol and diisobutene, wherein the methyl-tertiary-butyl-ether is contacted with the fixed bed cation exchange resin packing, in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt is the distillation
10 dissociation zone, followed by continuously withdrawing diisobutene and methanol from the distillation column reactor at a point below the feed zone of the methyl-tertiary-butyl-ether .

5. A method as claimed in claim 1, characterised by being a method of preparing diisobutene contacting a C₄ hydrocarbon stream containing isobutene with a fixed bed acid cation exchange resin packing thereby catalytically reacting isobutene with itself to form diisobutene, wherein the stream is contacted with a fixed
15 bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation zone, followed by continuously withdrawing at a point above the feed zone of the C₄ hydrocarbon stream containing isobutene and said diisobutene is withdrawn at a point below said feed zone.

6. A method as claimed in claim 1, characterised by being a method for separating isoolefins from a
20 mixture containing isoolefins and normal olefin by contacting the mixture with a fixed bed acid cation exchange resin packing thereby catalytically reacting isoolefin with itself to form a dimer, wherein the mixture is contacted with the fixed bed resin packing in a distillation column reactor the acid cation exchange resin beads being placed into a plurality of pockets in a cloth belt in the distillation zone while the resulting mixture of normal olefins and dimer is fractionated, and said dimer is withdrawn from said
25 distillation column reactor at a point below the feed zone of the mixture containing isoolefin and normal olefin.

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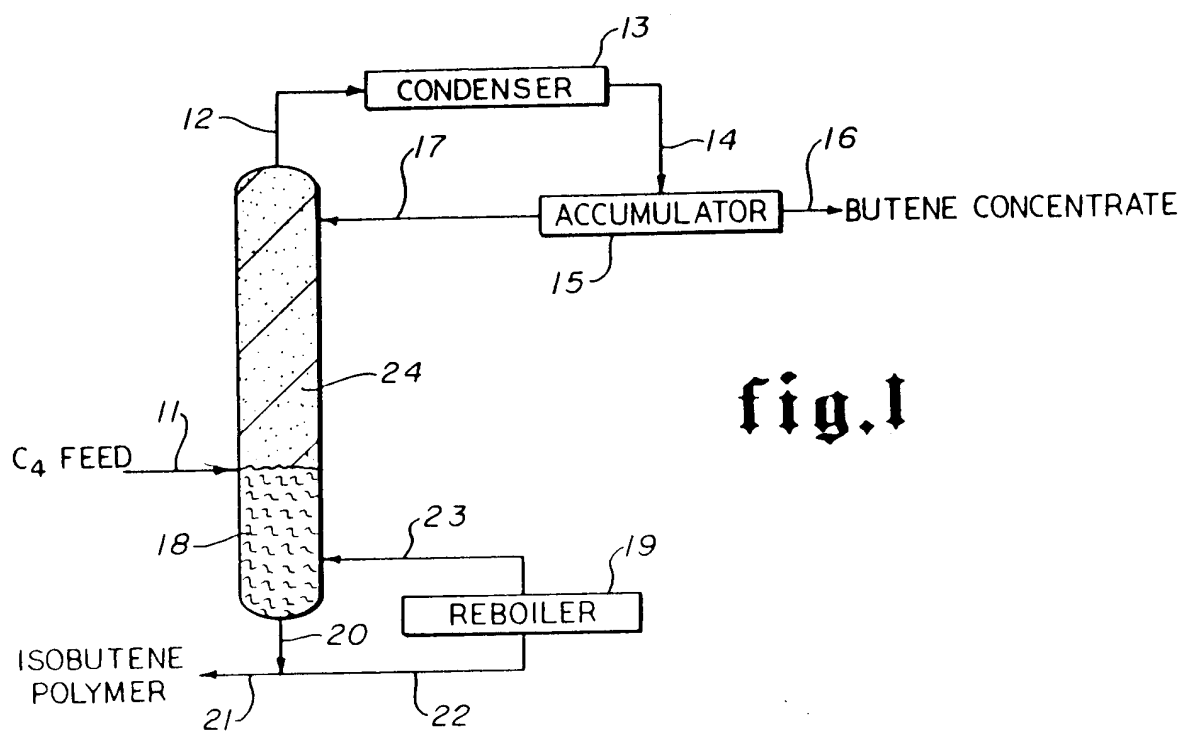


fig.1

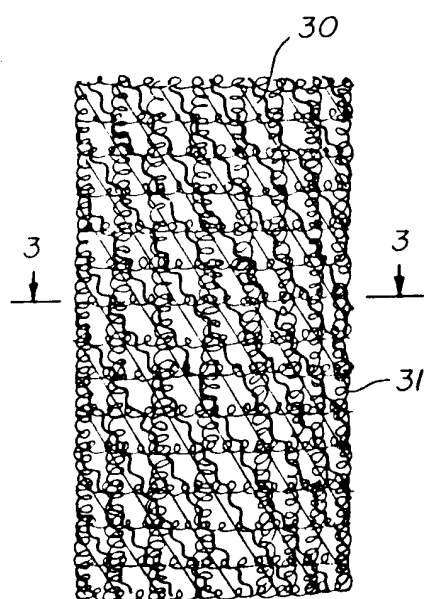


fig.2

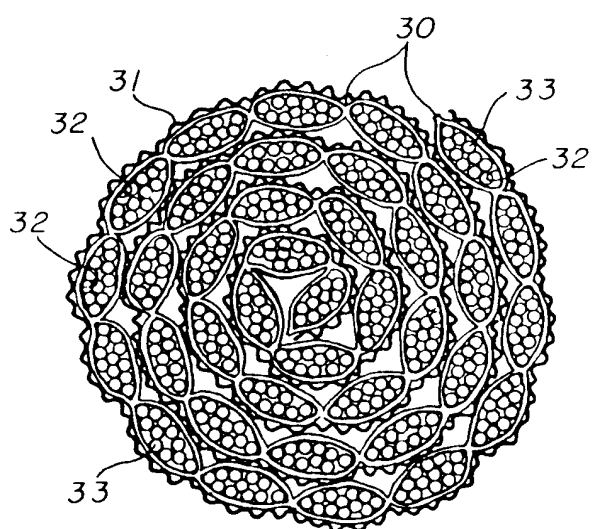


fig.3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 3680

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 008 860 (CHEMICAL RESEARCH AND LICENSING) * Pages 21-31; claims; figures * - - -	1-6	B 01 D 3/00 B 01 J 8/02 B 01 J 35/04 C 07 C 1/20 C 07 C 2/28 C 07 C 7/148 C 07 C 11/02 C 07 C 11/09 C 07 C 41/06 C 07 C 41/42 C 07 C 43/04
X	US-A-4 510 336 (D. HEARN) * Complete document * - - -	1	
X	US-A-4 504 687 (E.M. JONES) * Claims; column 5, line 58 - column 6, line 28 * - - - - -	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 D 3/00 B 01 J 35/00
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		24 April 91	WRIGHT M.W.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone</div> <div>Y : particularly relevant if combined with another document of the same category</div> <div>A : technological background</div> <div>O : non-written disclosure</div> <div>P : intermediate document</div> <div>T : theory or principle underlying the invention</div> <div>E : earlier patent document, but published on, or after the filing date</div> <div>D : document cited in the application</div> <div>L : document cited for other reasons</div> <div>& : member of the same patent family, corresponding document</div>			

DERWENT-ACC-NO: 1992-025870

DERWENT-WEEK: 199204

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TITLE: Catalytic distn. process for
chemical reactions using catalyst
particles in pockets of coiled
reinforced cloth belt

INVENTOR: SMITH L A

PATENT-ASSIGNEE: CHEM RES & LICENSIN[CHREN]

PRIORITY-DATA: 1990EP-113680 (July 17, 1990)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
EP 466954 A	January 22, 1992	EN

DESIGNATED-STATES: DE FR GB IT NL

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL- DATE
EP 466954A	N/A	1990EP- 113680	July 17, 1990

INT-CL-CURRENT:

TYPE	IPC DATE
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CIPS	B01D3/00	20060101
CIPS	B01J35/04	20060101
CIPS	B01J8/02	20060101
CIPS	C07C1/20	20060101
CIPS	C07C2/28	20060101
CIPS	C07C41/06	20060101
CIPS	C07C41/42	20060101

ABSTRACTED-PUB-NO: EP 466954 A

BASIC-ABSTRACT:

Chemical reactions are carried out in a distn. column contg. a catalyst. The catalyst particles are contained in a series of closed cloth pockets formed in a single cloth belt reinforced with wire mesh. The belt is coiled into a spiral so that the wire mesh is disposed between the coils.

The catalyst particles are pref. beads of acidic cation-exchange resin. The cloth pockets are sewn into a glass or PTFE fibre cloth belt wrapped in open-mesh knitted stainless steel wire.

USE/ADVANTAGE - The process is esp. useful for fractionating mixed butene streams by (a) reacting the isobutene with MeOH to form methyl t-butyl ether (MTBE), sepg. the MTBE from the n-butenes, and opt. converting the MTBE back to isobutene or to diisobutene, or (b) dimerising the isobutene and sepg. the diisobutene from the n-butenes. The catalyst system serves both as catalyst and as packing material for distn. @(17pp Dwg.No.0/3)

TITLE-TERMS: CATALYST DISTIL PROCESS CHEMICAL
REACT PARTICLE POCKET COIL
REINFORCED CLOTH BELT

DERWENT-CLASS: A41 E17 H02 J01

CPI-CODES: A01-D13; A04-G05; A10-B08; A12-M;
A12-W11K; E10-H01E; E10-J02C3;
E11-Q01; H02-A; H06-D04; J01-
A02A; N06;

CHEMICAL-CODES: Chemical Indexing M3 *01*
Fragmentation Code H5 H581 H8
M210 M211 M214 M233 M272 M282
M320 M416 M620 M720 N213 N262
N342 N441 Q110 Specific Compounds
R01568 Registry Numbers 1678

Chemical Indexing M3 *02*
Fragmentation Code H7 H721 M210
M214 M220 M222 M232 M233 M320
M416 M610 M720 N441 Q110 Specific
Compounds R00966 R02041 Registry
Numbers 7536 8014

Chemical Indexing M3 *03*
Fragmentation Code M423 M730 Q421

UNLINKED-DERWENT-REGISTRY- ; 0270S ; 0966S ;
NUMBERS: 0966P ; 1568P ; 2041P

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0037 0203 0206 0210 0223 0227
0229 0230 0231 0260 0266 0267
0281 0295 0306 0947 1123 2012
2020 2043 2065 2070 2124 2176
2189 2192 2206 2387 2392 2524
2541 2585 2676 2747 3162 3266

Multipunch Codes: 02- 03- 041 046 051 052 053 054
075 235 263 293 296 343 360 371
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689 723 726 020 022 022 022 026
026 028 029 204 206 207 217 218
219 220 238 267 326 039 04& 041
046 052 402 413 575 583 589 680
026 212 239 258

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 1992-011116